First X-Ray Structures of Ethylene Bridged Neutral Dimeric Hexacoordinate Silicon Complexes with Tetradentate Salen-Type Ligands

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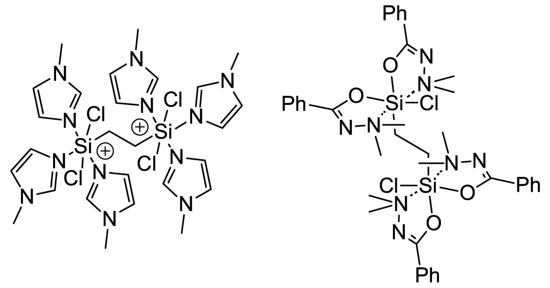
Syntheses and structures of two novel “doubledecker” silicon complexes [R-Si(*o*-O-*p*-OMe-C_6H_3-C(Ph)=N-$(CH_2)_2$-N=C(Ph)-C_6H_3-*p*-OMe-*o*-O)-CH_2-]$_2$ (R = Ph, *p*-*t*Bu-C_6H_4-O) with the silicon atoms hexacoordinated by two salen-type tetradentate ⟨*ONNO*⟩-chelating ligands are described. Hydrogen bonding between the halves of the bridged complexes as well as with chloroform solvate molecules determines the conformation. Compared with analogous mononuclear silicon complexes these ”doubledeckers” show bathochromically shifted Vis-absorption.

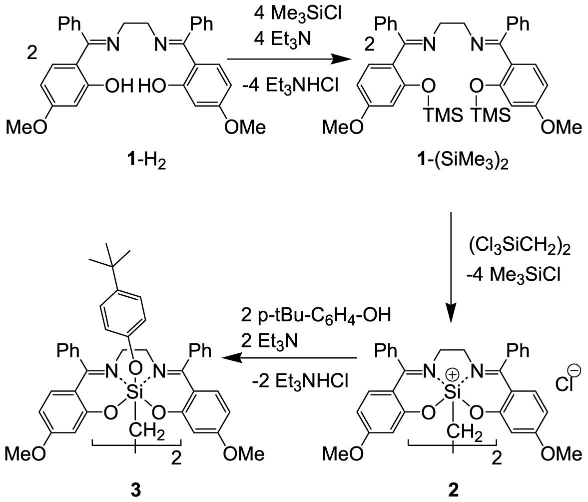
Key words: Doubledecker, Hexacoordinate, Hypercoordination, Schiff Base, Silicon

Introduction

Dinuclear hypercoordinate silicon complexes should provide representative molecules to study interactions between the linked coordination spheres. 1,2-bis(trichlorosilyl)ethane and 1,2-bis(phenyldichlorosilyl)ethane are suitable starting materials to synthesize model complexes. Up to now, four complexes with pentacoordinate [1 – 3] and only two with hexacoordinate [3, 4] Si atoms with a C_2-spacer between the central Si atoms were characterized by X-ray structure analysis. Those involving hexacoordinate silicon atoms (Scheme 1) offer quite flexible coordination spheres due to their mono- and bidentate ligands. Realizing the *cis*-orientation of the monodentate substituents should give rise to less sterical repulsion between the two halves of the complex.



Scheme 1.



Scheme 2.

Results and Discussion

Tetradentate chelating ligands of 2-iminomethylphenol type proved to be suitable for complexation of silanes leading to hexacoordinate silicon complexes with two *trans*-situated monodentate substituents [5, 6]. Reaction of the trimethylsilyl derivative of **1** with 1,2-bis(trichlorosilyl)ethane affords the silicon complex **2** exhibiting two pentacoordinate siliconium moieties [7]. This dinuclear building block was employed to synthesize **3** by addition of *p-tert*-butylphenol and elimination of HCl by triethylamine (Scheme 2).

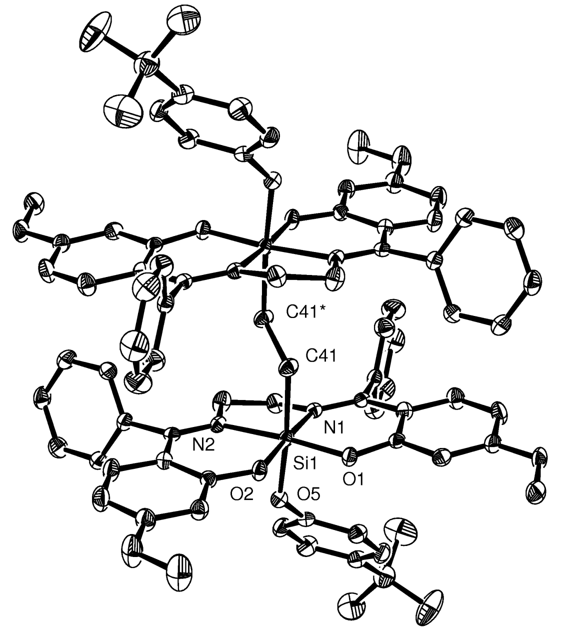


Fig. 1. Molecular structure of **3** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and chloroform molecules omitted for clarity. The molecule is situated on a crystallographically imposed inversion centre.) Selected bond lengths [Å] and angles [°]: Si1-C41 1.947(2), Si1-N1 1.929(2), Si1-N2 1.942(2), Si1-O1 1.762(2), Si1-O2 1.745(2), Si1-O5 1.799(2), C41-C41* 1.553(4), O5-Si1-C41 173.8(1), Si1-C41-C41* 123.2(2).

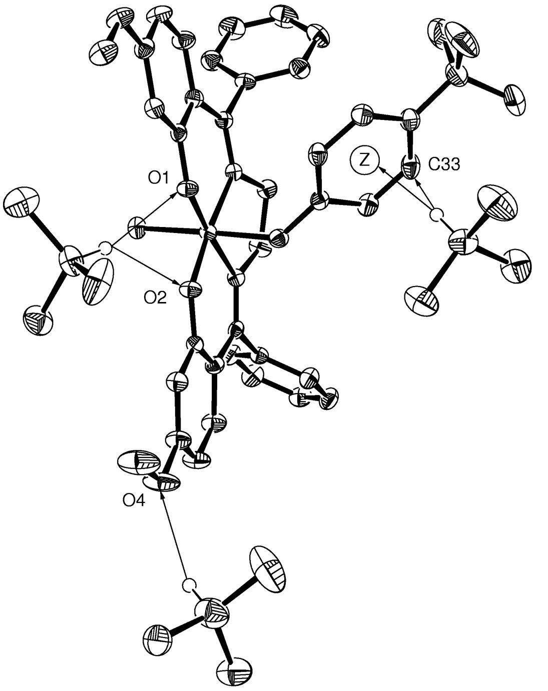


Fig. 2. One half of molecule **3** (hydrogen atoms omitted for clarity, centroid Z placed into the *p-tert*-butylphenolate ring).

The ionic state of **2** and its good solubility in chloroform allowed the stoichiometric conversion of this hypervalent silicon complex with *p-tert*-butylphenol into **3** in solution. Single crystals of **3** were grown from its chloroform solution. $\underline{\mathbf{3}}$*6CHCl$_3$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **3** in the unit cell. The two complex moieties are symmetrically arranged in the molecule (Fig. 1). The centre of the ethylene spacer (C41-C41*-bond) is situated on a crystallographically imposed inversion centre.

The coordination of the silicon atoms is nearly octahedral (O5-Si1-C41: 173.8(1)°; O2-Si1-N1: 174.55(8)°; O1-Si1-N2: 174.75(8)°) with the two monodentate substituents (*p-tert*-butylphenolate and alkyl groups) in axial positions. Surprisingly, the Si-C bond [Si1-C41: 1.947(2) Å] as well as the C-C bond of the ethylene spacer [C41-C41*: 1.553(4) Å] are not elongated significantly. The bond lenghts are identical with those found in the analogous mononuclear complex **1**-SiPhEt [6]. The planes of the two tetradentate ligand moieties are arranged anti-parallel without any discernible repulsive interactions. The bond angle Si1-C41-C41* [123.2(2)°] is remarkably large with respect to a tetracoordinate carbon atom. The ^{13}C NMR spectra of **3** confirm this deformation since C41 produces a signal at 33.8 ppm, significantly downfield-shifted with regard to data of sp^3-hybridized Si-bound CH$_2$ groups. However, this wide bond angle is not the result of the repulsion between the two chelating ligands: Even in **1**-SiPhEt [6] the corresponding angle is 123° at the Si-linked CH$_2$ group. Therefore, we can conclude that the repulsive interaction between the salen-type ligands and the carbon atom in β-position is determining the distance between the two silicon atoms. Referring to the other ethylene bridged silicon complexes [1–4], **3** has the largest angle at a spacer carbon atom found in such dinuclear compounds.

Besides these structural features, complex **3** shows interesting external bonding between the units in the crystal. The asymmetric unit contains three chloroform molecules with their positively polarized hydrogen atoms oriented towards electron rich sites (Fig. 2).

One chloroform molecule forms bifurcated hydrogen bonding with the chelating ligand's donor atoms O1 and O2 (distances H-O1 and H-O2: 2.535 Å each). The H atom of the second chloroform molecule points to the aromatic ring of the *p-tert*-butylphenolate lig-

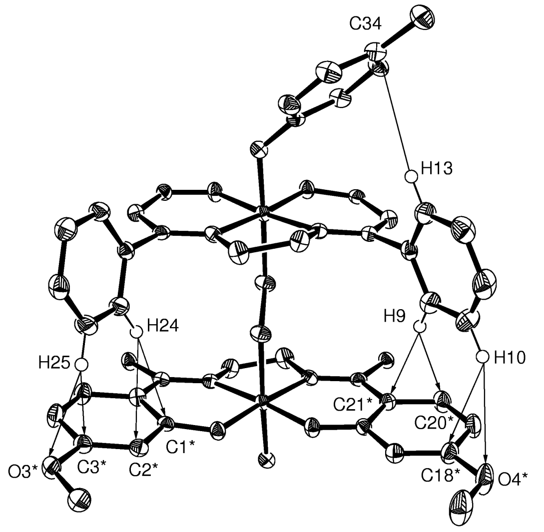


Fig. 3. Part of the molecule of **3** (most hydrogen atoms and chloroform molecules omitted for clarity). The shortest intramolecular hydrogen contacts are depicted by arrows.

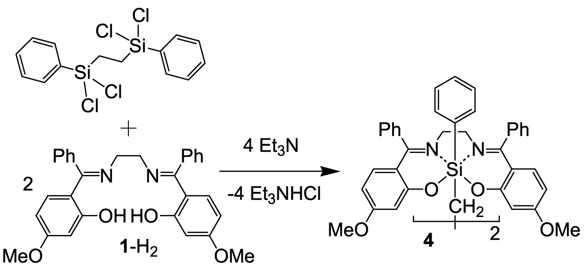
and (distances H-C33 and H-Z: 2.496 Å each). The third $CHCl_3$ molecule is twofold disordered, but the H atom clearly points to one of the salen-type ligand's two methoxy substituents (distance H-O4: 2.446 Å).

Between the aromatic systems of molecule **3** several intramolecular hydrogen contacts are established (Fig. 3).

These contacts between the two parallel tetradentate ligand moieties are in the range of 2.85 – 3.18 Å, allowing the conclusion that the interactions are attractive. In mononuclear hexacoordinate silicon complexes with ligand **1** the plane of the salen-ligand's phenyl substituent is perpendicular to the chelating plane and this conformation is also found in **3**.

According to an alternative route [6], the reaction of a dinuclear diorganodichlorosilane with ligand **1** yields the dinuclear diorganosilane **4** with hexacoordinate silicon atoms, which is also a "doubledecker" (Scheme 3). The X-ray structures of the educt and the product have been determined (Figs 4 and 5). (Suitable single crystals of complex **4** were grown from tetrachloroethane.)

1,2-bis(phenyldichlorosilyl)ethane crystallizes in the hexagonal space group $R\bar{3}$ with 9 molecules in the unit cell. The torsion angle Si1-C1-C1*-Si1* (180 °) indicates the staggered conformation of the molecule. The midpoint of the C1-C1* bond is located on an inversion centre, therefore maximum separation of the two bulky phenyl groups is achieved.



Scheme 3.

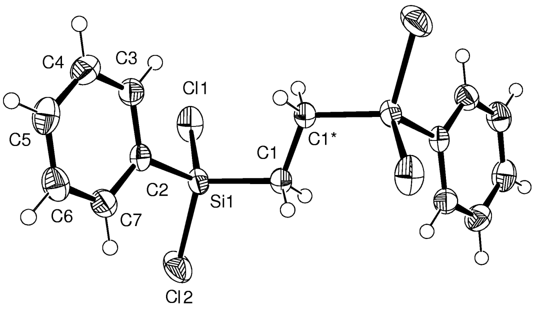


Fig. 4. Molecular structure of 1,2-bis(phenyldichlorosilyl)ethane (ORTEP plot with 50% probability ellipsoids). The molecule is situated on a crystallographically imposed inversion centre. Selected bond lengths [Å] and angles [°]: Si1-C1 1.853(1), Si1-C2 1.851(1), Si1-Cl1 2.0552(5), Si1-Cl2 2.0546(4), C1-C1* 1.539(2), C1-Si1-C2 114.46(5), Cl1-Si1-Cl2 108.26(2), Si1-C1-C1* 113.1(1).

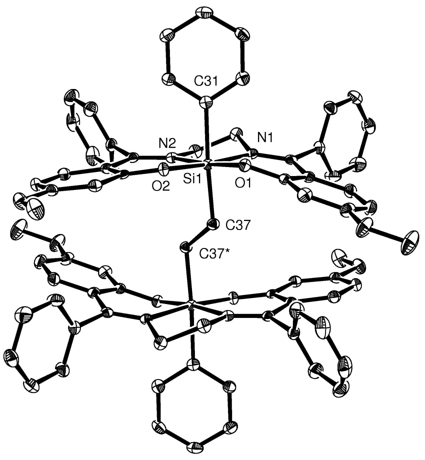


Fig. 5. Molecular structure of **4** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and tetrachloroethane molecules omitted for clarity. The molecule is situated on a crystallographically imposed inversion centre.) Selected bond lengths [Å] and angles [°]: Si1-C31 1.987(2), Si1-C37 1.946(2), Si1-N1 1.982(2), Si1-N2 1.994(2), Si1-O1 1.779(2), Si1-O2 1.776(2), C37-C37* 1.527(5), C31-Si1-C37 176.2(1), Si1-C37-C37* 122.4(2).

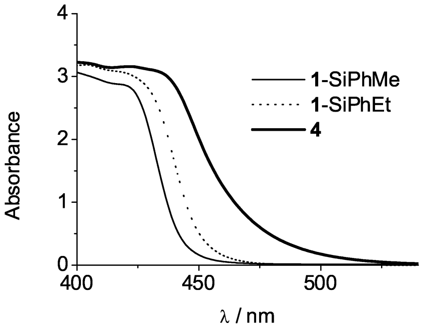


Fig. 6. Vis spectra of **1**-SiPhMe (0.01 mol/l), **1**-SiPhEt (0.01 mol/l) and **4** (0.005 mol/l) in chloroform ($d = 0.50$ cm).

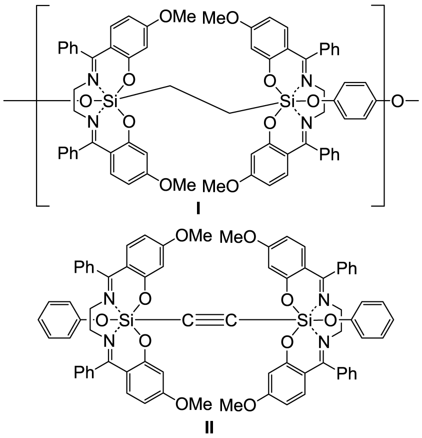
Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with 2 molecules in the unit cell. Analogous to **3**, the ethylene spacer of **4** is also positioned on a crystallographically imposed point of symmetry. The angle Si1-C37-C37* of the ethylene bridge is similar to that in compound **3** [122.4(2)° in **4**, 123.2(2)° in **3**], while the angle at the ethylene spacers' carbon atoms in the precursor with tetracoordinate silicon atoms is about 113°. Due to the repulsion between the salen-type ligands and the phenyl groups' ortho-hydrogen atoms, the planes of the chelating ligand moieties in **4** are not parallel.

Compound **4** is a suitable starting point to study the UV/Vis-spectroscopic behavior of such "doubledeckers". A comparison with the data of related mononuclear complexes **1**-SiPhMe and **1**-SiPhEt [6] is presented in Fig. 6.

Compounds **4**, **1**-SiPhMe and **1**-SiPhEt exhibit no distinct absorption bands in the Vis region but there is a remarkable bathochromic shift of a long wave shoulder [λ(**1**-SiPhMe) $<$ λ(**1**-SiPhEt) $\ll$ λ(**4**)]. Replacement of the methyl group in **1**-SiPhMe by the more electron-donating ethyl group gives rise only to a slight bathochromic shift of this absorption shoulder. This effect may either be due to the enhanced +I-effect of the ethyl group or the rehybridization of the alkyl-C-atom (123° at the sp^3-hybridized carbon atom!). The change in the absorption behavior between **1**-SiPhEt and **4**, however, is much more striking. It may be concluded that in **4** the two salen-type ligand moieties interact electronically which causes a narrow HOMO-LUMO-gap and a bathochromic shift of the Vis absorption.

Conclusions

Based on the present results, the synthesis of "multidecker" coordination polymers with salen type ligands (Scheme 4), starting from bifunctional siliconium salts and bifunctional phenols, should be explored. Investigations of the formation and spectroscopic as well as electronic properties of electronically coupled "double-" and "multidecker"-silicon complexes with salen-type ligands seem to be a promising route to a better understanding of special electronic effects in hypercoordinate silicon complexes.



Scheme 4.

In general, "doubledecker" silicon complexes with short spacers and aromatic ligands represent interesting model compounds for exploring π-π interactions between the ligand spheres ("molecular metals"). Up to now, only one of them – a bis(phthalocyaninato)tetrasiloxane with two O-bridged hexacoordinate silicon atoms and parallel arrangement of the macrocyclic ligand moieties – has been structurally characterized [8]. We expect that di- and oligonuclear hexacoordinate silicon complexes with salen-type ligands will provide further examples.

Experimental Section

All reagents were commercially available. All manipulations were carried out under an inert atmosphere of dry argon. Triethylamine was distilled from calcium hydride and stored over molecular sieve 3 Å. Chloroform (stabilized with amylene) was dried over molecular sieve 3 Å. NMR spectra were recorded on a BRUKER DPX 400 instrument ($CDCl_3$ solutions with TMS as internal standard). Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid. Vis spectra were recorded on a SPECORD S100 UV/vis spectrometer.

3: Triethylamine (1.0 g, 9.9 mmol) and *p-tert*-butylphenol (0.42 g, 2.8 mmol) were added to a stirred solution of **2** [7] (1.55 g, 1.40 mmol) in chloroform (10 ml) at ambient temperature to give a clear yellow solution. This mixture was stored at ambient temperature for 3 h

Table 1. Data of crystal structure determination and refinement of (**3**$*$6CHCl$_3$), (1,2-bis(phenyldichlorosilyl)ethane) and (**4**$*$4C$_2$H$_2$Cl$_4$).

Compound	**3***6CHCl$_3$	1,2-Bis(phenyldichlorosilyl)ethane	**4***4C$_2$H$_2$Cl$_4$
Empirical formula	$C_{88}H_{88}N_4O_{10}Si_2Cl_{18}$	$C_{14}H_{14}Si_2Cl_4$	$C_{82}H_{74}N_4O_8Si_2Cl_{16}$
T (K)	198(2)	203(2)	93(2)
Crystal system, space group	triclinic, $P\bar{1}$	hexagonal, $R\bar{3}$	monoclinic, $P2_1/c$
a (Å)	12.799(1)	19.4330(9)	11.7529(8)
b (Å)	13.013(1)	19.4330	19.3081(14)
c (Å)	14.5970(9)	11.9611(16)	19.2624(14)
α (°)	85.932(6)	90	90
β (°)	80.336(7)	90	107.462(4)
γ (°)	77.622(7)	120	90
V (Å^3), Z	2339.4(3), 1	3911.8(6), 9	4169.7(5), 2
ρ_{calc} (g cm^{-3}), μ (mm^{-1})	1.459, 0.611	1.453, 0.806	1.487, 0.614
$F(000)$	1058	1746	1916
Crystal size (mm^3)	$0.58 \times 0.22 \times 0.10$	$0.35 \times 0.23 \times 0.15$	$0.25 \times 0.10 \times 0.10$
$2\theta_{max}$ (°)	50	60	50
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-27 \le h \le 27$, $-27 \le k \le 26$, $-16 \le l \le 16$	$-13 \le h \le 13$, $-22 \le k \le 22$, $-22 \le l \le 22$
Reflections collected, R_{int}	72985, 0.0978	39674, 0.0263	56351, 0.0419
Independent reflections, parameters	8215, 582	2545, 91	7332, 589
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0394$, $wR_2 = 0.0824$	$R_1 = 0.0256$, $wR_2 = 0.0735$	$R_1 = 0.0390$, $wR_2 = 0.1030$
R Indices (all data)	$R_1 = 0.0713$, $wR_2 = 0.0901$	$R_1 = 0.0301$, $wR_2 = 0.0753$	$R_1 = 0.0573$, $wR_2 = 0.1106$
Largest diff. peak and hole (eÅ^{-3})	0.332, −0.311	0.475 and −0.454	0.729 and −0.669

to yield yellow crystals of **3**. The product was filtered off, washed with chloroform (10 ml) and dried in vacuum. Yield: 2.10 g (1.02 mmol, 73%) yellow crystals of **3***6CHCl$_3$. m.p. 153 °C (sealed capillary, not corrected). – ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.87$ (s, 4H, Si-CH$_2$-), 1.19 (s, 18H, -C(CH$_3$)$_3$), 3.27 (m, 8H, N-CH$_2$CH$_2$-N), 3.74 (s, 12H, -OCH$_3$), 6.00 (dd, 4H, ar, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.4$ Hz), 6.36 (d, 4H, ar, $^3J_{HH} = 8.8$ Hz), 6.43 (d, 4H, ar, $^4J_{HH} = 2.4$ Hz), 6.62 (d, 4H, ar, $^3J_{HH} = 8.8$ Hz), 6.72 (d, 4H, ar, $^3J_{HH} = 7.6$ Hz), 6.9 – 7.5 (mm, 20H, ar). – ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 30.5$ ((CH$_3$)$_3$*C*-), 31.7 ((*C*H$_3$)$_3$C-), 33.8 (Si-CH$_2$-), 48.7 (N-CH$_2$CH$_2$-N), 55.3 (-OCH$_3$), 103.9, 105.6, 114.5, 120.9, 124.9, 126.3, 127.2, 128.5, 128.7, 128.8, 134.2, 135.4, 139.8 (aromatic C-H, C-C), 157.9, 165.0, 165.3 (aromatic C-O), 169.0 (C=N). – ^{29}Si NMR (79 MHz, CDCl$_3$): $\delta = -172.3$, (79 MHz, CP/MAS): $\delta_{iso} = -170.8$. – $C_{88}H_{88}N_4O_{10}Si_2Cl_{18}$ (2055.90): calcd. C 51.41, H 4.31, N 2.73; found C 52.44, H 4.53, N 2.73.

1,2-Bis(phenyldichlorosilyl)ethane: The synthesis of this silane was already described in [9], but due to the bad yield (48.5%) of this literature method, it was carried out in a solvent (Me$_3$SiCl). – To trimethylchlorosilane (5 ml) a solution of H$_2$PtCl$_6$*6H$_2$O (50 mg) in 5 drops of isopropanol was added and stirred for 10 min. Then, phenylvinyldichlorosilane (3,00 g, 12,3 mmol) and phenyldichlorosilane (2,50 g, 14,1 mmol) were added and the mixture was stirred under reflux for 15 min. After cooling to room temperature the volatiles were removed under reduced pressure and the crude solid product was recrystallized from pentane. Yield: 2,60 g (6.84 mmol, 56%) nearly colorless crystals, m.p. 62 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.46$ (s, 4H, Si-CH$_2$-), 7.40 – 7.75 (mm, 10H, ar). – ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 12.5$ (Si-CH$_2$-), 128.5, 131.4, 131.9, 133.5 (*o*-, *i*-, *p*-, *m*- *ar*). – ^{29}Si-NMR (79 MHz, CDCl$_3$): $\delta = 18.9$. – $C_{14}H_{14}Si_2Cl_4$ (380.23): calcd. C 44.22, H 3.71; found C 43.91, H 3.74.

4: In 22 ml of chloroform, **1** (6.08 g, 12.7 mmol) and triethylamine (3,00 g, 29,7 mmol) were stirred at room temperature and a solution of 1,2-bis(phenyldichlorosilyl)ethane (2.41 g, 6.34 mmol) in 10 ml of chloroform was added dropwise. Within 3 d the chloroform solvate of **4** (**4**$*$2CHCl$_3$) crystallized from the resulting orange solution. It was separated by filtration, washed with 5 ml of a chloroform/hexane (4 : 1) and 10 ml of a chloroform/hexane mixture (2 : 3), and briefly dried in vacuum. (Upon drying the crystals easily collapse losing chloroform.) Yield: 8.10 g (5.65 mmol, 89%) orange powder of **4***2CHCl$_3$ (approximate stoichiometry) ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.22$ (s, 4H, Si-CH$_2$-CH$_2$-Si), 2.88 (m, 8H, N-CH$_2$ CH$_2$-N), 3.62 (s, 12H, -OCH$_3$), 5,95 (dd, 4H, ar, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.4$ Hz), 6.27 (d, 4H, ar, $^4J_{HH} = 2.4$ Hz), 6.42 (d, 4H, ar, $^3J_{HH} = 8.8$ Hz), 6.9 – 7.8 (mm, 30H, ar). – ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 30.9$ (Si-CH$_2$-); 48.5 (N-CH$_2$CH$_2$-N), 55.0 (-OCH$_3$), 104.0, 105.3, 115.1, 124.7, 126.3, 126.6, 127.1, 127.3, 128.8 (2×), 128.9, 132.5, 134.2, 135.6, 165.1, 165.4, 166.1 (ar), 169.5 (C=N). – ^{29}Si NMR (79 MHz, CDCl$_3$): $\delta =$

−167.6. – $C_{76}H_{68}N_4O_8Si_2Cl_6$ (1434.30): calcd. C 63.64, H 4.78, N 3.91; found C 61.78, H 4.73, N 3.85.

4*$4C_2H_2Cl_4$ was obtained by recrystallization from tetrachloroethane. – $C_{82}H_{74}N_4O_8Si_2Cl_{16}$ (1866.83): calcd. C 52.76, H 4.00, N 3.00; found C 54.15, H 4.28, N 3.11. (The systematically higher contents of C, H and N may originate from partial evaporation of tetrachloroethane from the crystals upon drying under vacuum prior to elemental analysis.)

X-ray analyses

X-ray structure data were recorded on a Bruker-Nonius-Kappa-CCD diffractometer (**3***$6CHCl_3$) and a Bruker-Nonius-APEX2-CCD diffractometer [1,2-bis(phenyldichlorosilyl)ethane and **4***$4C_2H_2Cl_4$] with Mo-K_α-radiation ($\lambda =$ 0.71073 nm) and semi-empirically corrected (SADABS). The structures were solved with direct methods (SHELXS-97) and refined by least squares methods (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined isotropically. Selected data of structure determination and refinement are presented in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-244226 (**3***$6CHCl_3$), CCDC-263779 (1,2-bis(phenyldichlorosilyl)ethane) and CCDC-263780 (**4***$4C_2H_2Cl_4$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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